December 2002

ELSEVIER

Materials Letters 57 (2002) 380–385

MATERIALS LETTERS

www.elsevier.com/locate/matlet

Effect of pH on the combustion synthesis of nano-crystalline alumina powder

L.C. Pathak*, T.B. Singh, S. Das, A.K. Verma, P. Ramachandrarao

National Metallurgical Laboratory, MTP Division, Jamshedpur 831 007, India

Received 20 March 2002; accepted 22 March 2002

Abstract

Synthesis of nano-crystalline alumina powder by a chemical pyrophoric reaction using citric acid and ammonia was investigated by varying the pH of the precursor solution, which played an important role in controlling the morphology of the synthesised powder. The flaky morphology obtained at pH = 2 could be modified to fine desegregated particulate form by varying the pH of the solution to 10. The sluggish decomposition rate at low pH was found to be responsible for the generation of flaky powders, whereas the rapid decomposition at high pH = 10 yielded the fine desegregated powders. The as-prepared powders were amorphous in nature, which yielded the nano-crystalline alumina powder after calcination at elevated temperatures.

Keywords: Nanomaterials; Ceramics; Alumina; Solution combustion process; Powder preparation; Nitrate–citrate process

1. Introduction

The solution based combustion synthesis of advanced materials, particularly the nano-crystalline ceramics and composites, has scientific as well as technological importance [1–3]. A series of such solution combustion decomposition (SCD) techniques are reported to yield single-phase products of various multi-component ceramics, where the heat generated during exothermic chemical reaction of combustion process is utilised to complete the phase formation of the products. Different chemicals such as, citric acid, urea, glycol, glycine, TFTA, etc., are normally being used as combustible agents for those combustion processes. The solution combustion technique using citric acid, which is widely known as amorphous citrate process, is a low-cost process. It uses readily available starting materials, namely metal nitrates with citric acid as complexing agent and is found to be highly promising in producing a variety of amorphous and nano-crystalline ceramic powders [4,5]. Though the solution combustion technique using citrate–ammonia route has been studied widely, very little effort has been made to study the various aspects of this process. Amongst them, the pH of the solution, temperature and composition of the solution are important. In this paper, the role of pH on the combustion synthesis of nano-crystalline alumina powder by a citrate–ammonia combustion technique is discussed.

* Corresponding author. Tel.: +91-657-43-1752; fax: +91-657-42-6527.

E-mail address: lokesh@csnml.ren.nic.in (L.C. Pathak).

0167-577X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0167-577X(02)00796-6

2. Experimental

Here, a simple and versatile process that utilises a pyrophoric chemical reaction to yield ultrafine ceramic powders was used to prepare nano-crystalline alumina powders. In this process, clear aqueous solution of $Al(NO_3)_3$ is prepared and calculated amount of citric acid was added. Subsequently, liquor ammonia was added to neutralise the pH of the solution at 7.0 and the final pH of the solution was adjusted at 2.0, 4.0, 6.0 and 10.0 by adding either dilute nitric acid or liquor ammonia as required. A pH meter from Aplab, India was used to monitor the pH of the solutions. The beaker containing the complexed solution was placed in a hot plate and heated to dry the liquid. The solution in the beaker was concurrently heated from the top by the radiation from an infrared lamp. During heating, the solution in the beaker was evaporated and a dried black-coloured gel-type mass was formed, which upon continued heating suddenly foamed up and caught fire, leaving a finely powdered mass in the form of a very low density sponge. The detailed process is given in the form of a flow sheet in Fig. 1.

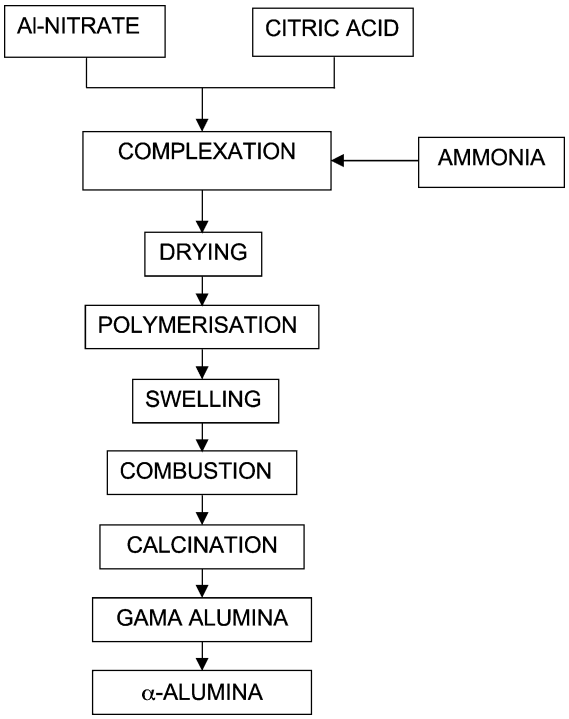

Fig. 1. Schematic of the nitrate–citrate combustion process.

The prepared powders were characterised by transmission electron microscopy (TEM), X-ray diffraction (XRD) and thermal analysis (TG and DTA) techniques. The dried semi-solid gel-type mass was collected prior to decomposition for all the pHs and investigated by the thermal analyser (TG/DTA). An equal amount of high-purity α-Al_2O_3 powder was used as the reference sample, and both the test and reference samples were heated at the rate of 10 °C/min during TG/DTA measurements. The as-prepared powders were calcined at various temperatures for a fixed period of 1 h. The calcined powders were characterised by TEM and XRD analyser. Carbon-coated copper grids were used to support the ultrasonically dispersed calcined powders for the TEM observations and nickel-filtered Co-Kα radiation was used for the X-ray diffraction analyses of the synthesised powders.

3. Results and discussion

During heating, the solution containing aluminium nitrate–citric acid–ammonia transforms into a semi-solid black-coloured gel-type mass, which on further heating auto-ignites to yield a charred mass. The appearance of the combustion decomposition is also evident from the thermal analysis (TG/DTA) of the dried mass collected prior to pyrophoric decomposition, which showed an exothermic peak at 288.41 °C with a concurrent weight loss of $\approx$ 85%. A typical TG/DTA plot for the sample obtained for pH = 10 is shown in Fig. 2. We have found that the combustion wave propagated from one point to the end point of the reactant and the combustion reaction is completed within a few seconds. Therefore, this solution combustion process can also be termed as solution combustion decomposition (SCD) technique. It is understood that the exothermic heat generated in this combustion technique is governed by a thermally induced redox reaction involving citrate and nitrate anions in the precursor, where the nitrate ions act as oxidant and the citrate ions act as reductant [6]. The possibility of this type of redox reaction can be understood from the comparison of the thermal analysis investigation of citric acid with the TG/DTA

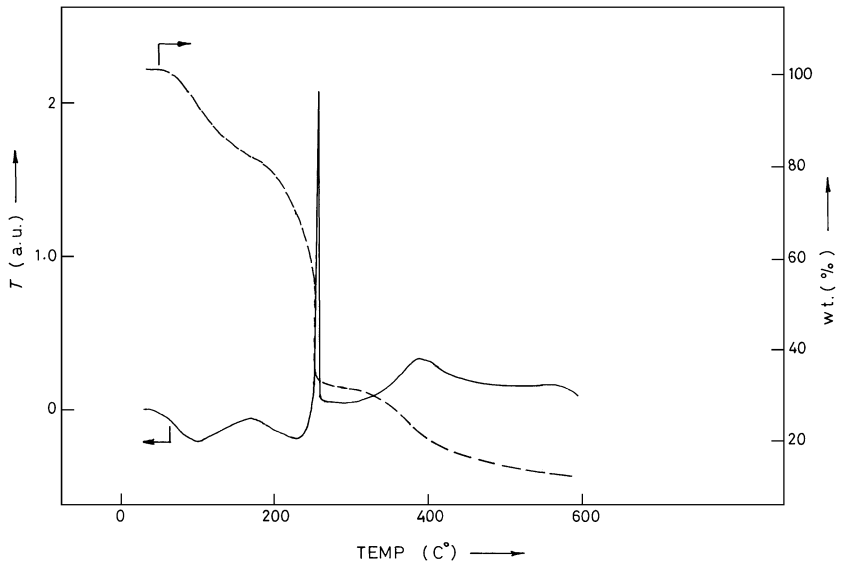

Fig. 2. TG/DTA plot of the nitrate–citrate precursor gel (pH = 10) collected prior to decomposition.

thermogram of the sample (Fig. 2). The thermal analysis of the citric acid was investigated by Hon et al. [7] and they have reported the appearance of one endothermic peak at ~ 300 °C and one exothermic peak at ~ 470 °C. The appearance of the exothermic peak at 288.41 °C for sample prepared at pH = 10 clearly indicates the nitrate–citrate redox reaction in this system.

The nitrate ions of NH_4NO_3 formed during addition of liquor ammonia by the following reaction

$$Al(NO_3)_3 + 3NH_4OH = Al(OH)_3 + 3NH_4NO_3 \quad (1)$$

and the citrate ions take part in this redox reaction. During heating, the citric acid melts at 173 °C and convert to aconitic acid by the reaction

$$C_6H_8O_7 \xrightarrow{175\ ^\circ C} C_6H_6O_6 + H_2O\ (g) \quad (2)$$

The aconitic acid then yields itaconic acid ($C_5H_6O_4$ and CO_2) on further heating. The itaconic acid (m.p. 166 °C), upon continued heating, undergoes polymerisation and swells with the de-carboxylation, releasing CO_2. The Al-hydroxide formed in the reaction (1) remains dispersed within the polymerised matrix and the heat liberated during exothermic redox reaction involving ammonium nitrate–citrate anions is found to be sufficient for the complete calcination of the compounds and water removal. The flash pyrolysis of

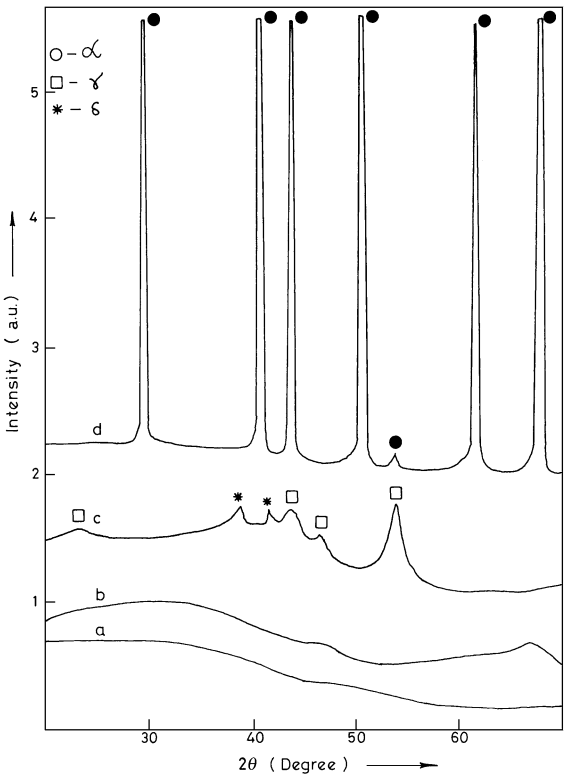

Fig. 3. XRD patterns of the alumina powder prepared from nitrate–citrate precursor (pH = 10): (a) as prepared, (b) calcined at 600 °C, (c) calcined at 700 °C and (d) calcined at 1200 °C.

NH_4NO_3 is known to yield nitrogen, H_2O and nascent oxygen [8], and this excludes the possibility of formation of NO_x and HCN species in the process, which makes the process less hazardous. The decomposed mixture after the completion of exothermic reaction was found to be a foamy mass and 3.5 g of the powder was observed to occupy a volume of 250 cm^{-3}.

The X-ray diffraction analyses of the as-prepared powder showed that the as-generated powders were amorphous in nature (Fig. 3a), which required to be calcined at elevated temperatures to yield α-alumina powder (Fig. 3d). The X-ray diffractogram of the as-prepared powders exhibits a prominent halo at $2\theta = 32°$, with half bandwidth $\Delta 2\theta_{1/2} \approx 10°$, at a scattering vector $\boldsymbol{k} = 19.35\ nm^{-1}$ (where $\boldsymbol{k}=(4\pi \mathrm{Sin}\theta)/\lambda$ and $\lambda = 0.179026$ nm is the X-ray wave length) and another relatively weak halo at 48°, intrinsic to an amorphous material [9]. A clear transition from amorphous state to nano-crystalline state could be noticed in the X-ray diffractogram of the powder calcined at 600 °C (Fig. 3b), where small and broad peaks started appearing at $2\theta = 48°$ and at $2\theta = 67°$. The amorphous alumina powder after calcination at 700 °C transform to γ-alumina and δ-alumina powder (Fig. 3c) and finally converts to α-alumina powder above 1100 °C. Single-phase α-alumina powder is prepared after calcination at 1200 °C for 1 h. Since all the organic materials and ammonia related compounds are either volatilised or burnt off during calcination at elevated temperatures, the purity of the alumina powder is controlled by the purity of starting chemicals.

The microstructural investigations carried out by the transmission electron microscope reveal that the pyrophorically generated powders are very fine and sub-micrometer in size at least in one direction. A few representative TEM images of the alumina powder prepared at different pHs are shown in Fig. 4. The transmission electron microscopy images showed a

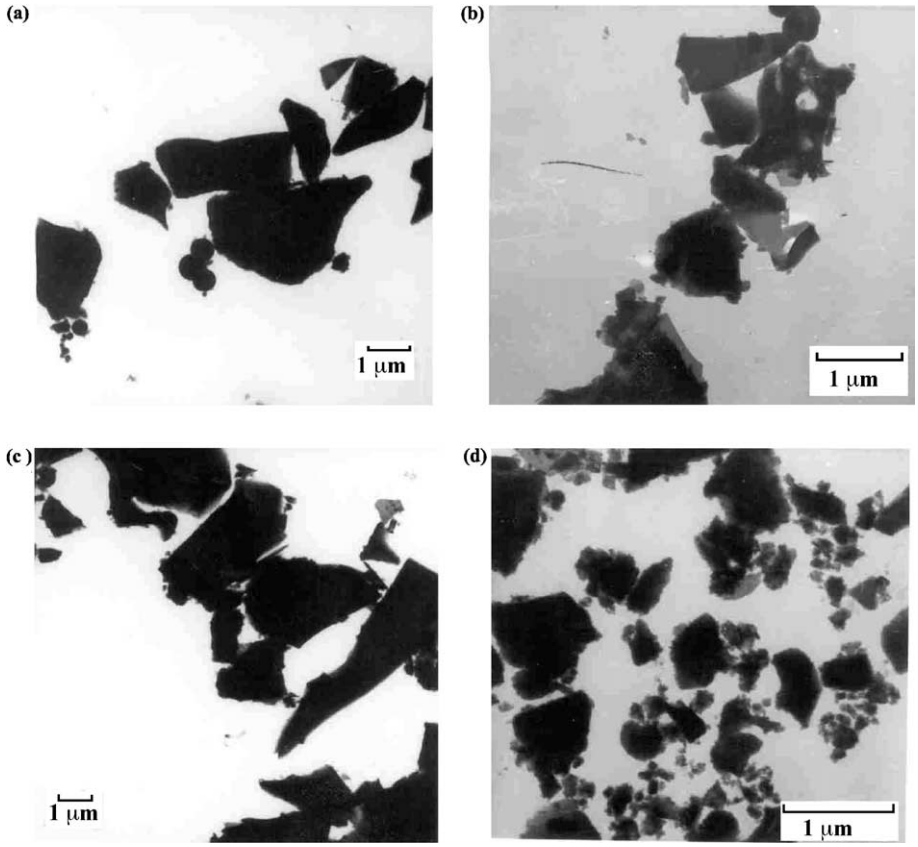

Fig. 4. TEM micrographs of the α-alumina powder prepared from nitrate–citrate precursors: (a) pH = 2, (b) pH = 4, (c) pH = 6 and (d) pH = 10.

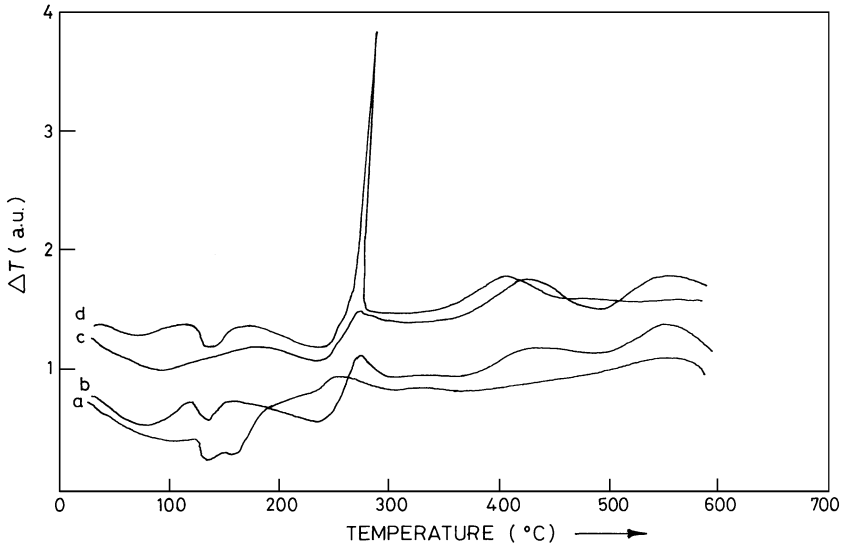

Fig. 5. DTA plots for the nitrate–citrate precursors: (a) pH = 2, (b) pH = 4, (c) pH = 6 and (d) pH = 10 collected prior to decomposition.

clear change in morphology as the pH of the solution increases from 2 to 10 (Fig. 4a–d). The particle morphology changes from plate-like flake structures (observed at low pH of 2) to desegregated fine particulates at pH = 10. The appearance of ring patterns in the electron diffraction of the flaky alumina powder (not shown in figure) indicates the polycrystalline nature of these flakes. The observation of electron diffraction in these flaky powders also indicate that the thickness of these flakes must be less than 200 nm; otherwise, the electrons could not be transmitted through thicker particles using 100-keV elec-

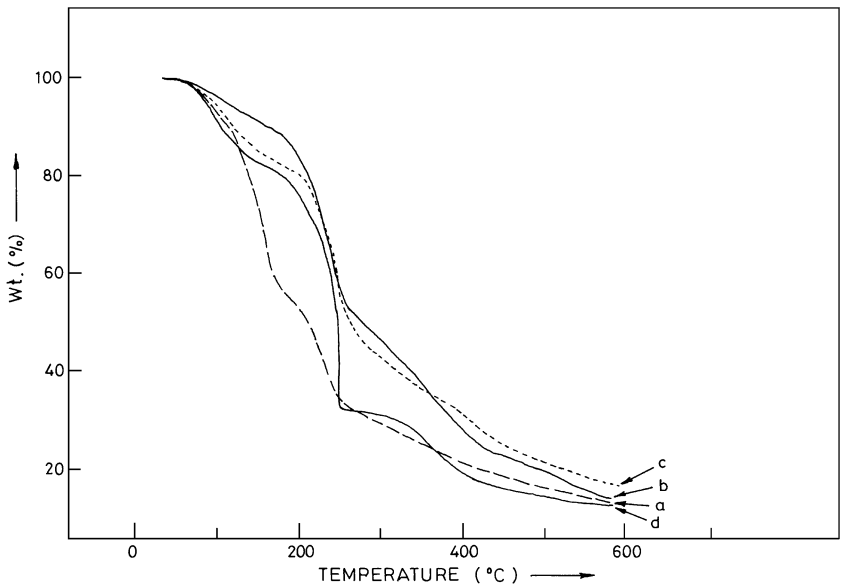

Fig. 6. TG plots for the nitrate–citrate precursors: (a) pH = 2, (b) pH = 4, (c) pH = 6 and (d) pH = 10 collected prior to decomposition.

tron beam in TEM. To understand the morphological variations of the synthesised powder with the solution's pH, we had carried out a detailed thermal analysis investigation on the gel-type precursors collected prior to combustion decomposition for all the pHs. The DTA plots for the samples showed that the nature of the exothermic peaks for the chemical decomposition reactions that takes place during heating of the samples changes with the pH of the solution (Fig. 5). The sharp decomposition of the precursors at pH 10 has been observed to be associated with a very sharp DTA peak (Fig. 2). The rapid pyrophoration at high pH of 10 has led to generation of large amount of gases, and such a vigorous process desegregates the precursor into ultrafine powders dispersed within the foamy structure. The exothermic peaks for the other pHs are relatively weak in nature (Fig. 6) and they are associated with slow rate of weight loss during heating (Fig. 6). The alterations of chemical compositions that were made to vary the pH of the solution precursor are possibly the reason for this decrease of exothermic peaks. It is known that citrate–nitrate stoichiometry in the precursor composition is the primary factor in controlling the reaction enthalpy in such a redox reaction [10]. If the oxidant ratio, i.e. nitrate ions in the precursor solution is increased in comparison to citrate ions, then the exothermicity of the reaction is reduced. In the solution, the citrate ion composition is fixed, whereas the nitrate ion concentration is varied by adding nitric acid to attain low pH values. Therefore, the increase of nitrate ions in the low pHs is expected to decrease the enthalpy of the exothermic reaction, which is in agreement with the experimental results. In the low pH values, the slow rate of decomposition of the precursor has enabled the alumina particles to come closer to form flakes.

4. Conclusions

A systematic investigation on the synthesis of nano-crystalline alumina powder by a chemical pyrophoric reaction using ammonia–citric acid route and by varying the pH of the precursor solution is carried out. The pH of the precursor solution plays an important role in controlling the morphology of the synthesised powder due to increase of nitrate ion concentration at low pHs. The sluggish decomposition of the precursors at low pH (2, 4 and 6) yielded flaky powders, whereas the rapid decomposition at high pH = 10 produced fine desegregated powders. The as-prepared amorphous powders yielded the nano-crystalline alumina powder after calcination at elevated temperatures.

References

[1] C.T. Chu, B. Dunn, J. Am. Ceram. Soc. 70 (1987) C375.
[2] C. Marcilly, P. Courty, B. Delmon, J. Am. Ceram. Soc. 53 (1970) 56.
[3] D. Bhattacharya, L.C. Pathak, S.K. Mishra, D. Sen, K.L. Chopra, Appl. Phys. Lett. 57 (1990) 2145.
[4] L.R. Pederson, G.D. Maupin, W.J. Weber, D.J. McReady, R.W. Stephens, Mater. Lett. 10 (1990) 437.
[5] S.K. Mishra, L.C. Pathak, V. Rao, Mater. Lett. 32 (1997) 137.
[6] J. Schafer, W. Sigmund, S. Roy, F. Aldinger, J. Mater. Res. 12 (1997) 2518.
[7] Y.M. Hon, K.Z. Fung, M.H. Hon, J. Eur. Ceram. Soc. 21 (2001) 515.
[8] C.A. Jackobson (Ed.), Encylopedia of Chemical Reactions, vol. V, Reinhold Publishing, New York, USA, 1953, p. 175.
[9] L.C. Chen, F. Spaepen, Nature 336 (1988) 366.
[10] A. Chkraborty, P.S. Devi, S. Roy, H.S. Maiti, J. Mater. Res. 9 (1994) 986.